#### INTEROFFICE MEMORANDUM

TO:

COMMISSIONER BRADLEY M. CAMPBELL

FROM:

ROBERT HAZEN, THOMAS MCKEE, STUART NAGOURNEY, A

THROUGH: EILEEN MURPHY PHD, DIRECTOR, DIVISION OF SCIENCE, RESEARCH AND

TECHNOLOGY

SUBJECT:

REVIEW OF NJDEP'S CHROMIUM CLEANUP CRITERIA FOR CHROMITE ORE-PROCESSING

RESIDUE SITES IN HUDSON COUNTY

DATE:

3/16/2004

We have reviewed the technical basis of the Department's current soil cleanup criteria for chromium. We have identified several areas where new information shows that there are errors and omissions in the Department's assessment of risk posed by chromium contamination at the chromite ore processing residue sites in Hudson County. These areas include the measurement of chromium, fate and transport assessment, modeling of human exposure, and impact to ground water assessment. Equally problematic are the generic "Alternative Remediation Standard Protocols" the Department has approved for responsible parties to develop site-specific soil cleanup criteria for chromium. The correction of these elements will lead to a substantial reduction in the numeric values used for cleanup.

The unusual chemistry of the chromite ore-processing residue (COPR) lies at the heart of many of the problems we have identified. Recent studies have illuminated this complex chemistry and have given us the basis for correcting the current problems. As an immediate measure we recommend that all chromium cleanup criteria be set using "total chromium", the only reliable measure of chromium in soils commercially available at this time. We further recommend that a level of 100 parts per million total chromium be used as a cleanup criterion until new criteria can be fully developed. Remedial action approvals should be limited to cleanup technologies that have been demonstrated to completely detoxify COPR such as the NJDEP certified Geotech Cold Top Ex-Situ Vitrification system. In March of 2002 the Department certified this system as an effective treatment technology to detoxify chromite ore processing residue.

# DRAFT REVIEW OF THE NJDEP SQIL CLEANUP CRITERIA FOR CHROMIUM

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#### **SUMMARY**

The current NJDEP cleanup criteria for chromium reflect the generic USEPA approach to risk assessment for trivalent chromium (CrIII) and hexavalent chromium (CrVI) and were first published in September 1998. There are numerous properties of chromite ore processing residue (COPR), however, which are important for predicting its human health risk that are not considered in the present criteria. COPR is the solid waste created by decades of chromium chemical manufacturing in Hudson County. Millions of tons of COPR have contaminated hundreds of sites in these highly urbanized areas. The applicability of the Criteria to these sites was a major focus of this review.

The NJDEP 1998 criteria (the Criteria) do not account for physical processes that concentrate CrVI by hundreds of times over bulk soil concentration. As applied, the Criteria do not set soil cleanup levels protective of ground water quality. The determination of compliance with the criteria relies on analytical methods that greatly underestimate the amount of CrVI in soil. The criteria do not account for the potential conversion of CrIII to the much more toxic CrVI. The Criteria neglect an important mechanism for CrVI to become airborne and contribute to a cancer risk from inhalation. Finally, the Criteria do not address the potential for contaminated groundwater to act as a vector for offsite transport of the chromium with resulting contamination of soil and structures.

#### INTRODUCTION

The Criteria are used by NJDEP for evaluation of chromite ore processing residue (COPR) sites. In response to a request by the Interfaith Community Organization a review of these criteria was undertaken to determine if recent research related to chromium risk assessment would have any potential effect on these numeric criteria.

There is a long history of guidance for developing soil cleanup criteria from the USEPA (USEPA 1996), which has been reiterated in numerous New Jersey statutes and regulations. Criteria development involves consideration of the inherent toxicity of the chemical and site conditions, which can lead to human exposure to the chemical by ingestion, inhalation, or skin contact. Criteria must take into account site-specific chemistry, available chemical analysis methods, comprehensive exposure analysis, and all relevant toxicities of the contaminant.

The Department's chromium cleanup criteria are shown in Table 1. This table is published on the NJDEP Site Remediation Program web site. It is the subject of the current review. The exposure pathways that are listed in Table 1 present a mixture of health endpoint (allergic contact dermatitis), biologic exposure routes (inhalation and ingestion) and route to a medium contamination (impact to groundwater) categories. Exposure pathways are not usually expressed with such a mix of concepts but non-the-less they can serve to explore the most important elements of the Department's risk assessment approach for chromium.

Table 1 also shows CrIII and CrVI have separately developed criteria which represents a change from the DEP's early guidance which was based on the more reliable measure of total chromium. Residential and nonresidential exposure scenarios present different activity patterns and therefore different exposures resulting in different cleanup criteria.

Threshold values such as those in Table 1, are considered inadequate for dealing with COPR sites in the United Kingdom. Recent research (Hillier 2003) on UK COPR sites concludes that: "... chemical analysis alone is no longer sufficient. ... information on processes occurring on sites and knowledge of the chemical associations and physical forms of contaminants is crucial." For New Jersey these important processes and physical forms of the contaminant are described in the present report.

# SITE SPECIFIC CHEMISTY AND CONDITIONS

#### Mobility of Hexavalent Chromium

The Chromite Ore Processing Residue (COPR) sites have unique characteristics, which complicate all stages of risk assessment analysis. Figures 1 and 2 illustrate the most important potential of the COPR sites to cause human exposure to carcinogenic hexavalent chromium. The yellow material, which appears on the inside of walls and stairs, is a concentrated form of hexavalent chromium that is present in a location of maximum concern for human exposure. The highly soluble CrVI moves dissolved in water as it slowly infiltrates the structure. The CrVI becomes concentrated as the water continually evaporates. This effect is seen on the surface of outdoor soil and has been observed a few feet below the surface of the soil where groundwater continually evaporates before it can reach the surface. Rainfall events and movement of groundwater levels can continually change the location of these highly concentrated evaporative fronts.

Appropriate cleanup criteria should account for this dynamic concentration process. The hexavalent chromium cleanup criteria shown in Table 1 (ranging from 20 to 6,100 ppm) reflect the final acceptable concentrations and do not reflect the potential for concentration as illustrated in Figures 1 and 2. For example if 20 ppm CrVI is present at a uniform concentration through out many feet of soil there is the potential for it to be transported to an evaporative front and become much more concentrated. Therefore, the Criteria would need to be reduced significantly to eliminate an unacceptable concentration. A recent analysis provides new information on how to estimate the concentration effect. This is presented in Appendix A.

# Leaching Behavior of Chromium from Waste Material

The chromite ore-processing residue has unusual properties, which should be considered for risk assessment and cleanup criteria development. Due to the widely differing toxicity of chromium depending on its valence state (CrVI or CrIII) the long-term stability of the valence state ratio in the waste material can influence the ultimate toxicity and potential to cause human exposure. There is new information from a Masters Thesis performed at the New Jersey Institute of Technology (Moerman 1996) to cause concern for the possibility that trivalent chromium may transform to hexavalent chromium over time given the known properties of COPR. Even if a small

fraction of the currently acceptable level of the 120,000-ppm of trivalent chromium (Table 1) becomes hexavalent chromium than a site will become more and more hazardous as time goes on. The Moerman thesis also examines the leaching properties of CrVI in COPR, which can confound accurate measurement of the amount of CrVI in the waste material using NJDEP specified methodology. These leaching properties were further illucidated by Scottish researchers (Hiller 2003). Detailed study of the chemistry and stoichiometry of chromium-bearing mineral phases in conjunction with phase abundance provides a quantitative description of the solid state speciation of Cr(III) and Cr(VI) in and amongst these minerals and in the COPR as a whole. This study provides insight into the processes that control the retention and release of Cr(VI) from COPR-contaminated sites. Such information is of particular value in risk assessment and in the development of methods of informed remediation.

#### COMPREHENSIVE EXPOSURE ANALYSIS

The pathways of contaminant transport from site to person must be completely characterized to obtain an accurate risk assessment. The ability of the contaminant to move from soil to groundwater can result in potential human exposure through either drinking water or other indirect means resulting from the transport of the chromium to previously uncontaminated areas. In Table 1 the effect on ground water is described as "site specific" and no numerical value of an acceptable concentration is given. The site-specific procedures were examined and are explained in Appendix D. It appears that while groundwater at sites is often measured and found to be above the trigger of 100ppb there is at present no approach to determining the concentration in soil which will prevent this. Groundwater as a vector for offsite transport of CrVI has not been addressed but could be estimated from the methodology in Appendices A and B.

The pathway of contaminated dust reaching human lungs is addressed for the residential and non-residential scenarios by the values of 270 and 20 ppm CrVI respectively in Table 1. However the Department also currently allows a site specific protocol which can lead to significantly higher levels being considered acceptable by up to thousands of times. This protocol eliminates an important part of the physical mechanism by which dust gets into the air and therefore can lead to an underestimate of risk. A further explanation and example is provided in Appendix E.

#### CONTAMINANT TOXICITY

#### Carcinogenicity

The Criteria do not consider CrVI a carcinogen by ingestion. There is, however, new information developed by New York University and others concerning the carcinogenicity of CrVI by ingestion. In addition, the National Toxicology Program is engaged in a thorough study of the carcinogenic potential of ingestion of CrVI. Currently CrVI is only considered to be carcinogenic by inhalation. This new research is presently under review by the Department's Division of Science, Research and Technology (DSRT). If CRVI proves to be a carcinogen by ingestion it will substantially lower the cleanup criteria.

# **Allergic Contact Dermatitis**

The Criteria include allergic contact dermatitis as an endpoint. The procedure for site specific allergic contact dermatitis criteria includes the assumption that CrVI must first be extracted into solution before it causes a response. This assumption results in a many fold increase in the acceptable concentration in soil. It should be noted that the state of Massachusetts uses this same endpoint in its chromium cleanup decisions and does not consider solublity to be necessary for an allergic response to occur.

# References

Hillier S. et al 2003 Role of quantitative mineralogical analysis in the investigation of sites contaminated by chromite ore processing residue The Science of the Total Environment 308:195-210

Moerman, E. 1996 <u>Advanced characterization and leaching behaviour of hexavalent and trivalent chromium from waste material</u> Thesis, New Jersey Institute of Technology, Department of Civil and Environmental Engineering

USEPA 1996 Soil Screening Guidance: User's Guide EPA Document Number: EPA540/R-96/018 July 1996

Table 1

# SOIL CLEANUP CRITERIA PROPOSED SEPTEMBER 18, 1998

EXPOSURE PATHWAY	TRIVALENT CHROMIUM		HEXAVALENT CHROMIUM			
	RESIDENTIAL SCENARIO	NONRESIDENTIAL SCENARIO	COMMENT	RESIDENTIAL SŒNARIO	NONRESIDENTIAL SŒNARIO	COMMENT
ALLERGIC CONTACT DERMATITIS	NONE	NONE	1	UNDER DEVELOPMENT	UNDER DEVELOPMENT	4,5
INHALATION	NONE	NONE	2	270 PPM	20 PPM (PRELIMINARY)	4,6
INGESTION	120,000 PPM	NOT REGULATED	3	240 PPM	6,100 PPM	
IMPACT TO GROUND WATER	NONE	NONE	1	SITE SPECIFIC	SITE SPECIFIC	5,7

- 1- Under normal environmental conditions, trivalent chromium is insoluble in water. Therefore, exposure via this pathway is not relevant.
- 2 Toxicological data for trivalent chromium does not exist for this exposure pathway. Therefore, soil cleanup criteria cannot be established.
- 3 For the nonresidential scenario, ingestion of trivalent chromium does not pose an unacceptable risk. Therefore, a soil cleanup criterion is not prop
- 4 Exposure models and assumptions have been developed or are being finalized; generic soil cleanup criteria are being developed.
- 5 Soil cleanup criterion will be the same for both the residential and nonresidential scenarios.
- 6 Due to the effects of vehicular traffic, the nonresidential scenario soil cleanup criterion will be lower than the residential scenario soil cleanup crite
- 7 Due to highly variable soil conditions throughout the State, it is not possible at this time to develop a generic impact to ground water cleanup criter

Figure 1 Chromate Bloom 1



Figure 2 Chromate Bloom 2

